



Preparation and Electrical Properties of Dense Ceramics with NASICON Composition Sintered at Reduced Temperatures

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Abstract. A reduced temperature route is explored for the preparation of ceramics with NASICON composition. The procedure includes sol-gel synthesis, Sample Controlled Thermal Analysis of the precursor powders and hot-pressing the powders under 0.3 GPa and at temperatures between 600 and 900°C. It is shown that ceramics with densities around 90% can be obtained by this route. Electrical conductivity values and activation energies are determined and discussed.

Keywords: ionic conductors, hot-pressing, thermal analysis, electrical conductivity

1. Introduction

NASICON is a well-known crystalline sodium ion conductor with a composition $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ ($0 < x < 3$) [1] that is especially used in electrochemical sensors for liquid [2] and gaseous environments [3, 4]. The NASICON structure is formed by ZrO_6 octahedra, connected by SiO_4 or PO_4 tetrahedra. The sodium ions occupy two different sites in the crystal lattice: one formula unit is fixed and the excess sodium ions (x) are at interstitial sites, where they possess a large mobility in the 3D channels of the NASICON structure. The large interstitial cation concentration and their high mobility induce an important ionic conductivity even at relatively low temperatures. For example at 300°C, conductivity values of about 10^{-1} S/cm are obtained. [5]

A major problem of NASICON electrolytes is however the difficulty of preparation of phase-pure ceramics; especially the solid state preparation requires high temperature treatments, typically at 1200°C (very close to the melting point of NASICON), and

the loss of sodium often leads to the appearance of ZrO_2 as a second phase. Sol-gel techniques [6, 7] have been investigated to improve phase purity and sinter ability. [8] However, obtaining dense, fine-grained NASICON is impossible with any of the reported processing methods. Our aim is trying to achieve the fabrication of dense, nano-sized NASICON materials to investigate the effect of grain size on the electrical properties of a Na ion conductor. In the present work, we explore a “nano-route”, based on low temperature processing steps only. This procedure includes sol-gel synthesis of precursors, thermal treatment at reduced temperature to eliminate solvent and volatile components, densification to ceramics by hot-pressing, and, finally, assessment of the electrical properties of the obtained materials.

2. Experimental

2.1. Sol-Gel Synthesis

Precursor powders with nominal composition $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ were prepared by a sol-gel technique described by Shimizu et al. [7] High purity reagents

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(Aldrich) were used without further purification: 0.69 g $\text{NH}_4\text{H}_2\text{PO}_4$, 4.5 g $\text{ZrO}(\text{NO}_3)_2 \cdot 8\text{H}_2\text{O}$ and an excess of 1.46 g Na_2SiO_3 were dissolved in water and stirred at room temperature for 2 hours. The pH was then adjusted to 3 by adding HNO_3 and the solution heated to 60°C for 3 hours. The viscous gel was finally dried at 110°C during 12 hours.

2.2. Sample Controlled Thermal Analysis

The precursor powder was treated using a Sample Controlled Thermal Analysis (SCTA) route. In this technique, the heating rate is adapted to keep a physical

parameter, here the pressure of evolved gases, constant. The procedure was described in detail elsewhere [9, 10]. The residual pressure above the sample was maintained at 1 Pa until a final temperature of 600°C was reached. The quantity of sample used was about 0.1 g. The totality of the gaseous decomposition products was monitored by quadrupole mass spectrometry (VC quadrupole).

2.3. Hot-Pressing

The hot-press used was a prototype (Cyberstar, Grenoble, France), which was described elsewhere [11]. The

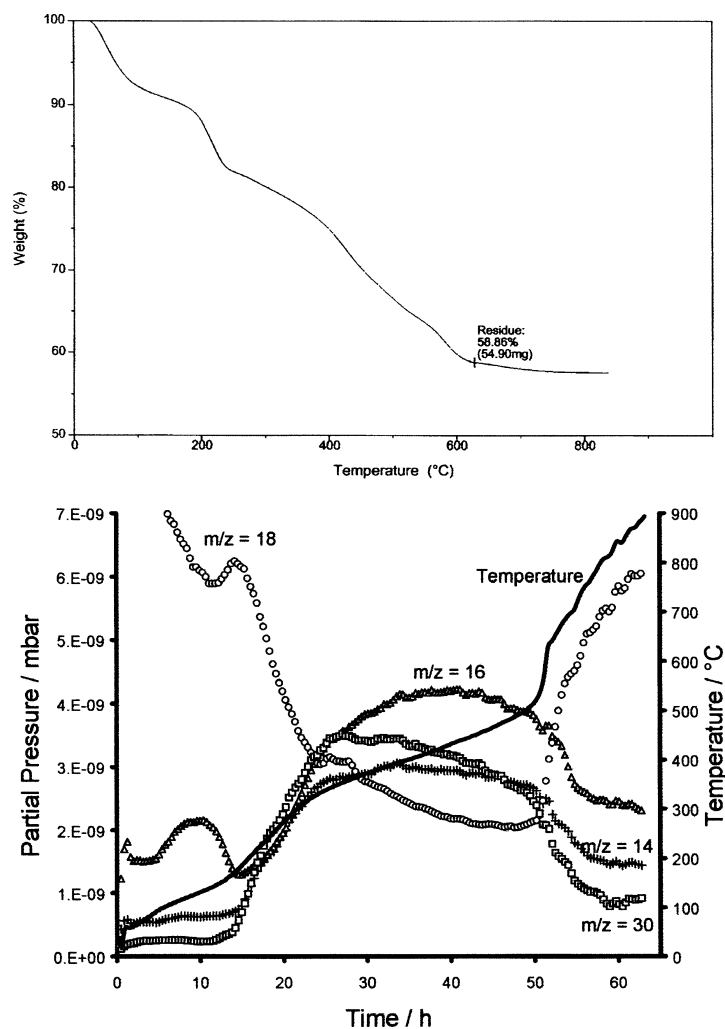


Fig. 1. Controlled rate thermogram of precursor powder (top) and mass spectrometric analysis of decomposition products (bottom) m/z : 14 (N), 16 (O), 18 (H_2O), 30 (NO).

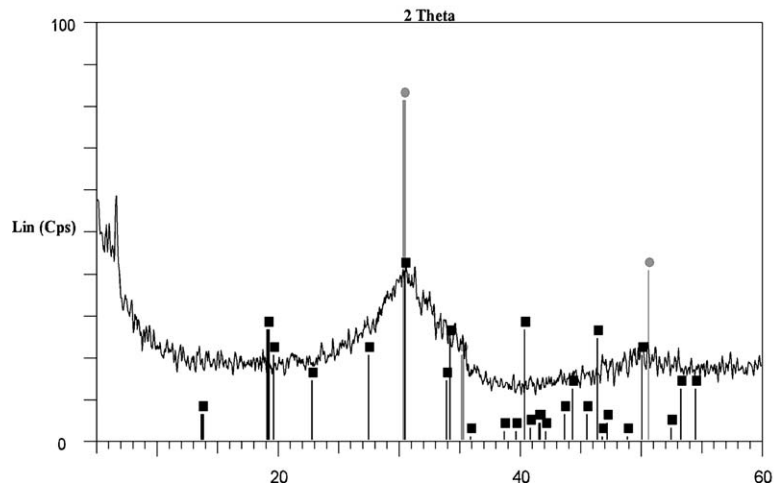


Fig. 2. X-ray diffraction pattern of the precursor powder after thermolysis. (■) Nasicon (hexagonal, JCPDS no33-1313), (●) ZrO_2 (tetragonal, JCPDS no42-1164).

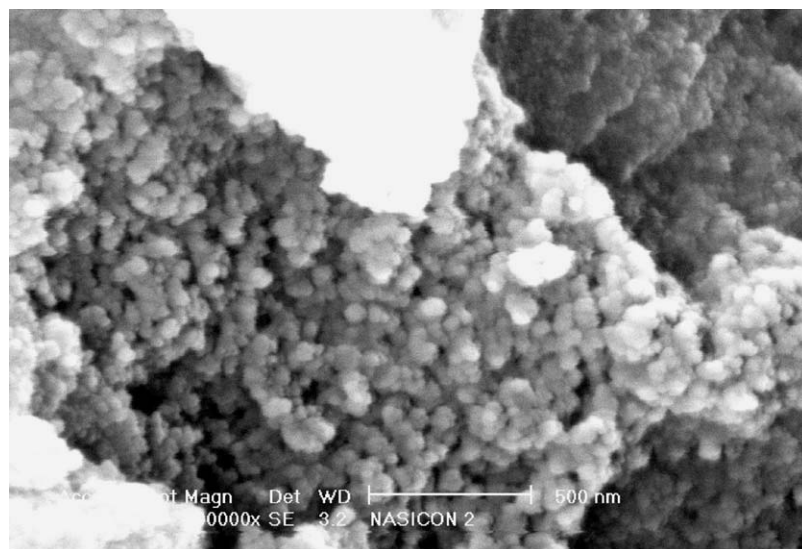


Fig. 3. Scanning Electron Micrograph of the precursor powder after thermolysis.

precursor powder treated by SCTA was introduced in pure alumina dies and pressed under 0.3 GPa. The heating rate was 5 K/min until the plateau temperature was reached where the sample was kept 2 hours. Three plateau temperatures were investigated: 600, 750, and 900°C. The evolution of density could be monitored *in situ* by dilatometry.

2.4. Characterization of Structure, Density and Electrical Conductivity

The structure of the samples was investigated at all preparation stages by usual characterization techniques: X-ray diffraction (D5000 diffractometer, Siemens) and Scanning Electron Microscopy

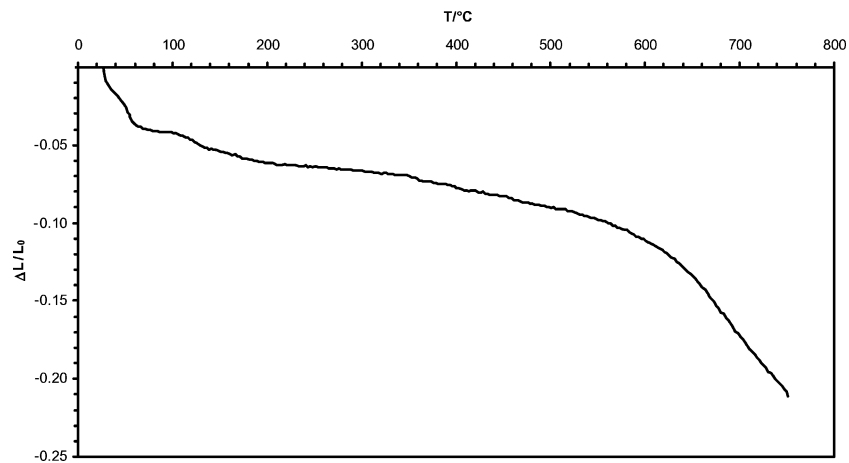


Fig. 4. In situ dilatometric curve during hot-pressing with a plateau temperature at 750°C.

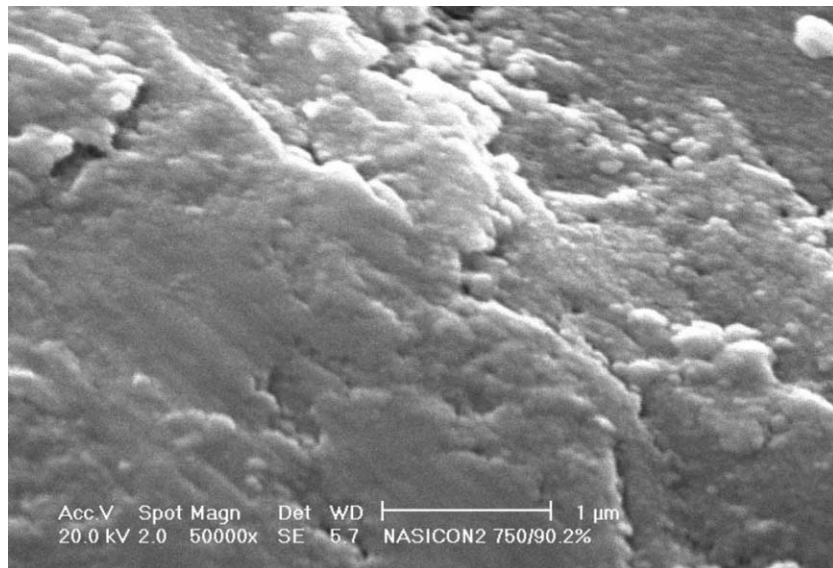


Fig. 5. Scanning Electron Micrograph of a pellet hot-pressed at 750°C.

(Philips XL30 ESEM and Cambridge instruments S90). The density of the samples was determined from mass and geometrical dimensions and using Archimedes' technique. The electrical properties were measured by Impedance Spectroscopy (EG&G, model 6310) in the frequency range between 10^{-1} and 10^5 Hz under pure argon.

3. Results and Discussion

3.1. Sample Controlled Thermal Analysis (SCTA)

Figure 1 shows the evolution of the sample mass during SCTA. One can notice several steps, where the mass loss is particularly large. The respective decomposition product can be identified using mass spectrometric

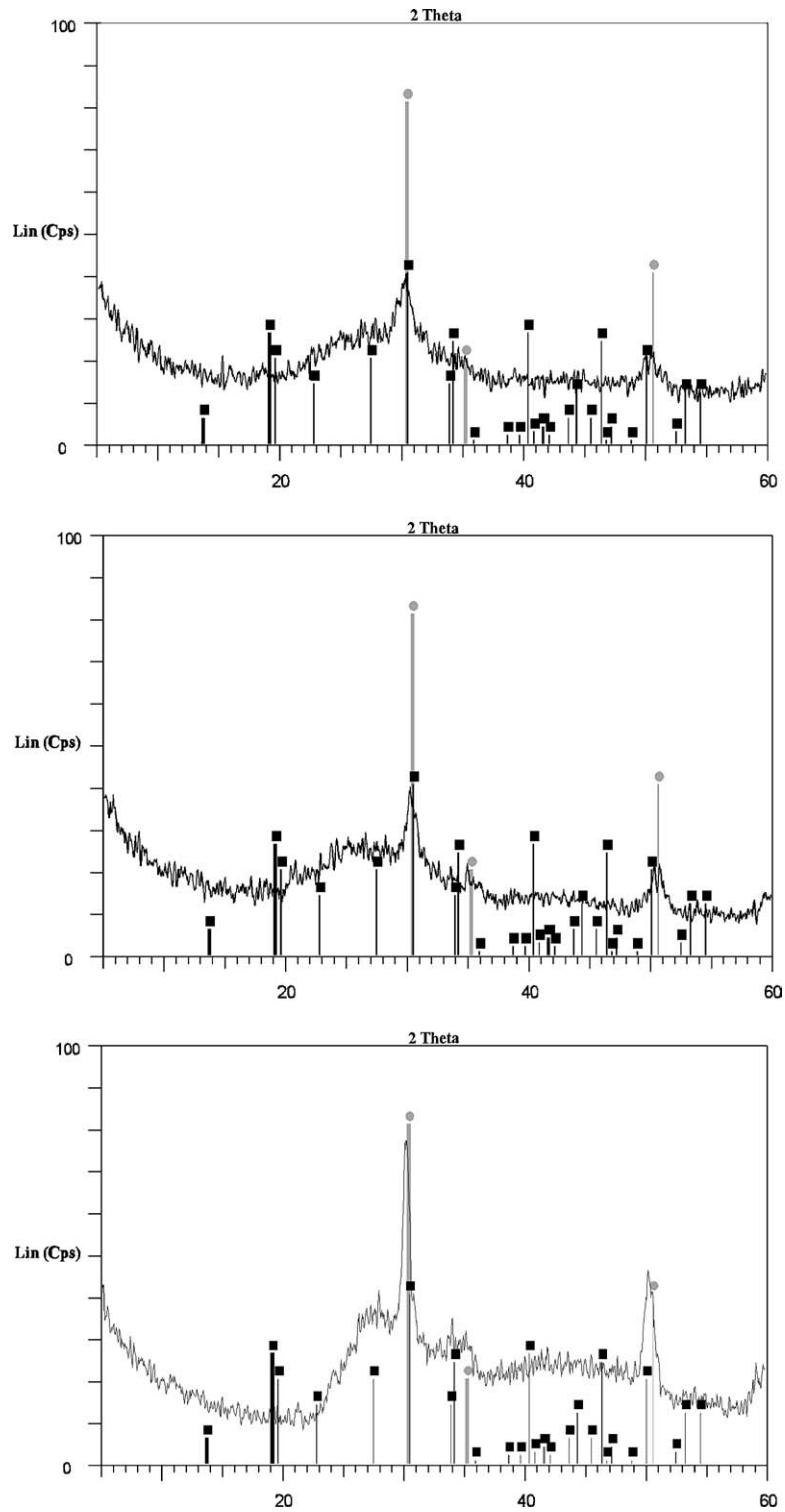


Fig. 6. X-ray diffraction pattern of dense pellets hot-pressed at 600 (top), 750 (middle) and 900°C (bottom). (■) Nasicon (hexagonal, JCPDS no.33-1313), (●) ZrO₂ (tetragonal, JCPDS no.42-1164).

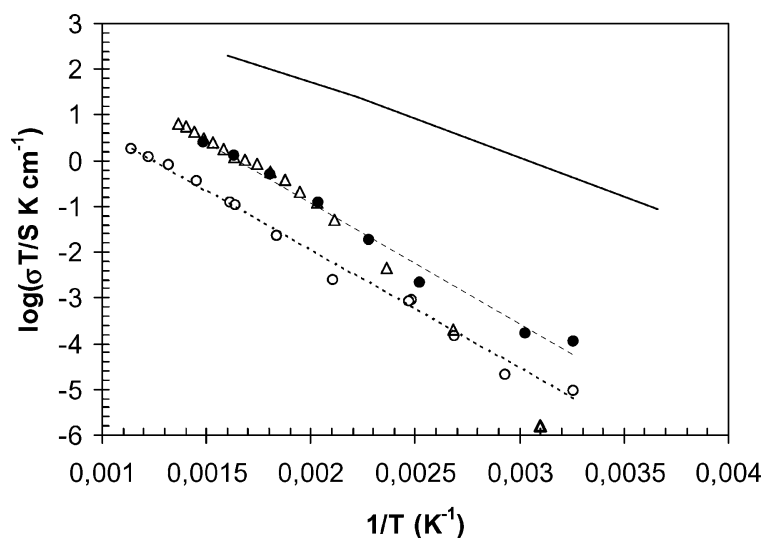


Fig. 7. Electrical conductivity of ceramics with NASICON composition, obtained by hot-pressing at 600 (Δ), 750 (\circ) and 900°C (\bullet) and comparison with literature data (full line [5]).

analysis. The mass loss below 200°C can be attributed to the removal of more or less strongly bound water molecules, adsorbed or constitutional, whereas between 200 and 600°C NO evolution, due to the decomposition of nitrates, is predominant. This can be concluded from the simultaneous increase of the traces for NO, N and O fragments. The removal of volatile components is essentially complete at 600°C, where a total mass loss of more than 40% of the initial mass is observed. The X-ray diffraction pattern of the sample after removal of volatile components is shown in Fig. 2: the broad diffraction line around the NASICON reflection indicates an amorphous phase, without major amounts of crystalline compounds. The microstructure observed by Scanning Electron Microscopy is presented in Fig. 3. Small agglomerated particles with a mean particle size of about 60 nm are visible. This is in contrast with materials prepared at this temperature by traditional thermal methods where significant crystallization occurs. The fact that this material prepared via SCTA is amorphous has important implications with respect to the following treatment with the hot press.

3.2. Densification by Hot-pressing

Figure 4 shows a typical dilatometric curve using the amorphous precursor treated by SCTA; in this case,

the plateau temperature was 750°C. Sintering is observed above 600°C; the final density of such pellets was in the range $(90 \pm 2)\%$ of the theoretical density of $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ (3.27 g/cm^3). A Scanning Electron Micrograph of a hot-pressed pellet with 90% density is presented in Fig. 5. At 600°C, densities above 80% could be obtained by this procedure and at 900°C, the average density attained $(93 \pm 3)\%$. This appears very satisfactory for such temperatures of operation. The mean particle size in the dense pellets remains low: an average particle size of 120 nm is for example obtained at 750°C. Grain growth could thus be kept at a low level, compared with the usual high temperature sintering. The phase evolution for 600, 750 and 900°C was monitored by X-ray diffraction (Fig. 6). One notices the presence of crystalline NASICON already at 600°C and increasing amounts of crystalline phase at 750 and 900°C. Crystallization of NASICON prepared by the usual sol-gel technique was previously reported to occur around 880°C [12]. A small amount of tetragonal zirconia is observable at 750°C and very clearly at the highest temperature 900°C, where it was also confirmed by Raman spectroscopy. Tetragonal ZrO_2 was previously reported to be formed at 1200°C using the same precursor, but not treated by SCTA [12]. The stabilization to lower temperatures versus monoclinic structure might be related to the high pressure during hot-pressing and the small particle size.

3.3. Electrical Properties

Figure 7 shows a conductivity comparison of ceramics hot-pressed at 600, 750 and 900°C with literature data [5]. The phase transition between monoclinic and rhombohedral crystalline NASICON, which gives a kink in the conductivity data, was not apparent in our samples, showing that the amount of crystalline phase was still small. The electrical conductivity remained below literature data for crystalline NASICON. A similar activation energy was found, about 50 kJ/mol (0.5 eV), which is higher than the value observed in totally crystalline materials (30–35 kJ/mol) [13–15]. Both results indicate a more difficult ionic motion in our samples. One can estimate that the particularly favorable ionic conduction channels existing in the crystal lattice are not percolating and that the ionic motion is partially hindered in the disordered amorphous structure.

It is interesting to notice that above 250°C the samples hot-pressed at 600°C present approximately the same conductivity as the samples sintered at 900°C and are clearly more conducting than the 750°C samples, although the activation energy is the same. This indicates that the predominant conduction mechanism is similar in all cases. One can argue that the formation of poorly conducting ZrO₂ particles above 600°C, as shown by the XRD patterns (Fig. 5), blocks the ionic motion and annihilates the expected conductivity increase at higher temperature. From the present results, it appears that the electrical properties of ceramic samples prepared at the lowest temperature are the most encouraging and it is clearly worth continuing their investigation.

4. Conclusions

We have explored a reduced temperature route to prepare highly dense materials with NASICON composition. Sample Controlled Thermal Analysis was used to gently remove volatile components from the precursor and hot-pressing to make pellets with high density. The electrical properties were compared with crystalline

NASICON. The amorphous structure is less conductive and presents higher activation energy, indicating less favorable conditions for ionic motion in this phase. However, the lower processing temperature might be advantageous for large scale preparation of materials for sensor applications.

Acknowledgments

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